# CORRELATION OF THE pH OF A COAL-METHANOL/WATER SOAK WITH COKE STRENGTH AFTER REACTION WITH $CO_2$ (CSR)

David H. Buchanan and Kenneth J. Coombs

Chemistry Department
Eastern Illinois University
Charleston, IL 61920

Hardarshan S. Valia

Inland Steel Flat Products Co., Research Laboratories,
East Chicago, IN 46312

Keywords: Coke Strength After Reaction (CSR), Weathering Index, pH Coal Slurry

## ABSTRACT

Weathering of coals during storage at coke plants leads to a decrease in coke quality and an increase in operating costs for iron making. Coke Strength After Reaction with $CO_2$ (CSR) is an important measure of coke quality for blast furnace operation. This study was undertaken to predict changes in CSR values of coke caused by weathering of coals during storage. CSR values of coke were compared with a variety of feed coal properties, including pH of a methanol/water soak. The results indicated that an increase in coal oxidation resulted in a drop in pH of methanol/water soak. CSR generally dropped with a drop in pH for all the coals. However, good correlation existed between CSR and pH for lower rank (high volatile) coals.

## INTRODUCTION

At Inland Steel Flat Products Company, the improvement in CSR had a major stabilizing influence on blast furnace operation.(1) The CSR is primarily dependent on the plastic properties of coal which are known to deteriorate with oxidation of coal.(2-4) Hence, a research program was initiated to decipher how coal oxidation affects coke quality, especially CSR, and cokemaking operations. The primary objectives were to develop means for measuring coal oxidation and to learn how to interpret these measurements in ways useful to the coke plant operators.

Although documentation exists detailing the relationship of coal oxidation to coke properties, little information has been published regarding the effect of coal oxidation on hot strength properties of coke. Crelling, et al. (5) correlated coke reactivity to the amount of weathered coal in the mix. The reactivity increased with an increase of weathered coal in the mix; however, the reactivity was measured through the Bethlehem method. Huffman, et al. (6) reported loss in coke reactivity for the most highly weathered Pittsburgh seam (VM = 36.2%, db) coal; the coke reactivity was measured as percent of coke reacted after 2 hours at 1000 °C in $CO_2$. Pis, et al. (7) reported an increase in coke reactivity with increase in coal oxidation under accelerated oxidation conditions; the reactivity was measured through the ECE method. Price, et al. (8) indicated a decrease in CSR for a western Canadian coal after storage in barrels for 20 weeks.

Because an appreciable portion of coal used in the coking industry is stored in large piles for various periods of time, it was appropriate to study the deterioration in coal properties due to natural weathering and assess its effect on coke properties, especially CSR, and cokemaking. In this paper, only the statistically significant correlations between CSR and pH of methanol/water soak are discussed. The effect of weathering on other properties of coke and cokemaking operations are discussed more fully elsewhere.(9)

## EXPERIMENTAL

Six piles, 3 tons each, of each of the coals that were in use at Inland, were made in the open yard at the Research pilot facility. The coals were Coal A (High Volatile), Coal B (High Volatile), Coal C (High Volatile), and Coal D (Medium Volatile). The analytical data for the fresh coals are given in Table I. Pile No. 1 was the base fresh coal and was subjected to carbonization in Inland's 565 kg movable-wall pilot oven with interior dimensions of 1,143 mm high x 1,219 mm long x 457 mm wide.(10) The operational data summary for the carbonization tests is given elsewhere.(2) Also, a wet charge of 30% Coal A, 30% Coal B, and 40% Coal D was carbonized in the pilot oven for coals from the respective piles. CSR and other coke quality parameters were measured. The CSR was determined through the NSC method. Coke quality data, from the pilot oven carbonization of fresh coals, are also included in Table I. Pile Nos. 2 to 6 were carbonized after 35 days, 70 days, 105 days, 180 days, and 420 days of natural oxidation, respectively. The coals from each pile were subjected to the following analyses: rheological, proximate, ultimate, alkali solubility, petrography, pH (methanol/water soak), FTIR-PAS, and sole-heated oven (SHO) analysis. For the pH measurements, HPLC grade methanol and Milli-Q™ purified water (resistance > 16 M$\Omega$) were used. A 25 mL aliquot of 20% (v/v) methanol/water was pipetted into a 50 mL Erlenmeyer flask containing 2.000g coal. The flask was closed with a rubber septum cap fitted with gas inlet and outlet needles and nitrogen gas bubbled through the slurry for 20 minutes. Placing the flask in an ultrasonic bath maintained at 25 Deg.C improved coal wetting. A septum cap with an all-glass pH electrode inserted through a hole was placed on the flask and the pH measured after equilibrating the electrode for 10 minutes in the slurry. The Orion Research Model 710 pH meter was calibrated with buffers prepared in 20% methanol/water at pH 4 and 7.

## RESULTS AND DISCUSSION

### 1) Change in pH with Time

Figure 1 shows plots of pH measurement of methanol/water soak for individual coals; measurements were not made for the blend. For all coals, there is a rapid drop in pH for the first 2-3 months. Beyond this time, the drop is generally insignificant. A drop in pH with oxidation has been reported in literature.(11-13) It is also apparent that the pH of methanol/water soak from fresh Coal A is distinctly acidic (possibly due to the combination of lower rank, higher microporosity, and higher sulfur content) and with oxidation, it becomes more acidic due to the release of sulfur and acids produced from coal oxidation reactions. It is known that lower rank coals produce more acidic products during weathering.(13) The pH of methanol/water soak from the fresh Coal D, Coal C, and Coal B is distinctly basic, and the pH value drops with an increase in oxidation. Thus, both the absolute value and the change in pH are coal dependent.

The reproducibility of the pH measurements on triplicate samples was = 0.07 units. Because particle size has an significant effect on the pH of the slurry it is important to standardize the grinding of coal samples for these measurements for sample to sample consistency. Data in Table 2 are for a -8 mesh, weathered Illinois No. 6 coal (River King Mine) which was ground in a nitrogen-flushed ball mill and separated into size fractions by sieving. The pH of the larger particles is lower than that of the smaller particles. A sample of the same River King coal which had been ground to -100 mesh prior to weathering had a pH of 5.02 compared to the pH of 5.36 found for the -100 mesh fraction of the coal weathered as larger particles. These results indicate that the surfaces exposed in grinding had been protected from oxidation and had developed fewer acidic groups than surfaces on the un-ground larger particles. The observed differences in pH values of the unweathered coals may be a function of the mineral matter composition of each coal.

2) Change in CSR with Time

Figure 2 shows variation in CSR with weathering time for all individual coals and blends.(9) CSR in all cases decreases with an increase in weathering time. The drop in CSR was most dramatic during the first few months of summer exposure; thereafter, the CSR generally decreased with time or there was little change in CSR.

Using the highest and lowest CSR values, and not the trend lines, it can be deduced that the magnitude of CSR drop is highest for the lowest rank Coal A, followed by the blend, Coal B, Coal D, and Coal C. The CSR dropped by about 24 points for Coal A, 19 points for the blend, 13 points for Coal B and D, and 8 points for Coal C. The large drop in CSR for the blend may be due to a combination of higher amount of Coal A and higher amount of oxyvitrinite from Coal A, Coal C, and Coal D. It is interesting to note that Coal D, a medium volatile rank, undergoes oxidation-induced loss in CSR by the same amount as the high volatile Coal B. The Coal C is least susceptible to weathering-induced CSR loss.

3) Correlation of Change in pH to CSR

The changes observed in this study were for a small 3-ton pile. Different natural conditions exist in large coal piles, hence, the time period may not be applicable when the results are applied to the large commercial piles. Hence, it is important to come up with a coal oxidation monitoring device that directly relates to coke properties and can be monitored constantly in the pile. With this premise, the changes in coal quality were correlated to coke quality. The increase in coal weathering resulted in deterioration in CSR and was accompanied by a drop in pH of methanol/water soak.

Figure 3 shows the correlation between the pH of coal-methanol/water soak and the CSR for all the coals. CSR generally drops with a drop in pH for all the coals. However, good correlation exists between CSR and pH for Coal A and Coal B (the lower rank high volatile coals). It was reported elsewhere that for Coal C and Coal

D (the borderline high volatile/medium volatile coal, and medium volatile coal) the fluid temperature range, (as determined through Gieseler plastometer) correlated well with CSR.(9) This relationship can be used to predict CSR of lower rank (high volatile) coals by monitoring pH.

## APPLICATION

On the basis of results from this study, a coal oxidation monitoring plan for the lower rank (high volatile) coal has been devised as follows:

1) Obtain the pH of the incoming coals from the respective mines.

2) Identify the placement of incoming coals in the coke plant yard.

3) Monitor the drop in the pH of coal in the coal piles.

4) Estimate the loss in CSR by using a set of graphs that depict a drop in pH versus a drop in CSR. Figures 4 shows one such example.

5) Once the coal oxidation has affected CSR in such a way that the target CSR is not met, as indicated through the drop in pH, then the usage of oxidized coal in the blend should be redefined.

6) If new high volatile coals are brought in, the graphs of a drop in pH versus CSR could be developed while monitoring the new coal pile and verifying the results through pilot oven carbonization.

## CONCLUSIONS

On the basis of this study, the following conclusions can be made:

1) An increase in coal weathering resulted in a drop in pH of methanol/water soak.

2) An increase in coal weathering resulted in a drop in CSR and the drop in CSR can be correlated to a drop in pH of coal methanol/water soak.

3) pH measurement can be used as a quality control tool for monitoring weathering of low rank (high volatile) coals that are characterized by low fluid properties.

## ACKNOWLEDGEMENT

Partial support of this work by the Council on Faculty Research at Eastern Illinois University is gratefully acknowledged. H.S.V. would also like to acknowledge the assistance of several colleagues at the Inland Steel Research Laboratory for their assistance with various aspects of this work.

## REFERENCES

1) Valia, H.S., et al., "Production and Use of High CSR Coke at Inland Steel Company," ISS-AIME Proc., Vol 48, 1989, pp. 133-146.

2) Valia, H.S., "Prediction of Coke Strength After Reaction with $CO_2$," Iron and Steelmaker, May 1989, pp. 77-87; also to be published in Iron & Steel Soc. Trans., Vol 11, 1990.

3) Schmidt, L.D., "Changes in Coal During Storage," in "Chemistry of Coal Utilization," Lowery, H.H., (Ed), Vol. I, 1945, John Wiley & Sons, N.Y., pp. 627-676.

4) Gray, R.J. and Lowenhaupt, D.E., "Aging and Weathering," in "Sample, Selection, Aging, and Reactivity of Coal," Klein, R. and Wellek, R. (ED.), 1989, John Wiley & Sons, N.Y., pp. 255-334.

5) Crelling, J.C., et al., "Effects of Weathered Coal on Coking Properties and Coke Quality," Fuel, Vol. 58, 1979, pp. 542-546.

6) Huffman, G.P., et al., "Comparative Sensitivity of Various Analytical Techniques to the Low Temperature Oxidation of Coal," Fuel, 1985, Vol. 64, pp. 849-856.

7) Pis, J.J., et al., "Effect of Aerial Oxidation of Coking Coals on the Technological Properties of the Resulting Cokes," Fuel Processing Technology, 1988, Vol. 20, pp. 307-316.

8) Price, J.T., et al., "Effect of the Properties of Western Canadian Coals on Their Coking Behavior," ISS-AIME Proc., 1988, Vol. 47, pp. 39-55.

9) Valia, H.S., "Effects of Coal Oxidation on Cokemaking," ISS-AIME Proc., 1990, Vol. 49.

10) Kaegi, D.D. and Osterman, C.A., "The Use of Illinois Coal for the Production of High Quality Coke," ISS-AIME Proc., 1980, Vol. 39, pp. 239-248.

11) Gray, R.J., et al., "Detection of Oxidized Coal and the Effect of Oxidation on the Technological Properties," SME-AIME Trans., Vol. 260, 1976, pp. 334-341.

12) Mikula, R.J. and Mikhail, M.W., "A Delta P Technique for the Prediction and Monitoring of Coal Oxidation," Coal Preparation, 1987, Vol. 5, pp. 57-69.

13) Yun, Y., et al., "Attempted Development of a 'Weathering Index' for Argonne PCSP Coals," Am. Chem. Soc. Div. Fuel Chem. Preprints, 1987, Vol. 32, No. 4, pp. 301-308.

Table I. Analyses of coals and their cokes

| | Coal A | Coal B | Coal C | Coal D | Blend 30%A 30%C 40%D |
|---|---|---|---|---|---|
| Petrographic Analysis | | | | | |
| Total Inerts (%) | 7.61 | 16.76 | 20.62 | 20.29 | 14.55 |
| Oxyvitrinite (%) | 0.0 | 0.0 | 0.60 | 0.20 | 0.20 |
| Pseudovitrinite (%) | 0.60 | 0.40 | 0.20 | 0.60 | 0.40 |
| Mean Max. Vitrinite Reflectance (%) | 0.67 | 0.90 | 1.07 | 1.35 | 1.04 |
| Alkali Extraction (%, Transm.) | 97.0 | 96.0 | 99.0 | 97.0 | 98.0 |
| Proximate Analysis (%, db) | | | | | |
| Volatile Matter | 35.7 | 31.2 | 27.1 | 23.2 | 27.7 |
| Fixed Carbon | 58.7 | 62.3 | 67.0 | 71.7 | 66.9 |
| Ash | 5.6 | 6.5 | 5.9 | 5.1 | 5.4 |
| Sulfur | 1.11 | 0.56 | 0.82 | 0.8 | 0.87 |
| Alkali Index | 1.98 | 0.81 | 1.82 | 1.89 | 1.56 |
| Free Swelling Index | 3.0 | 7.5 | 8.0 | 7.5 | 5.0 |
| Ultimate Analysis (%.db) | | | | | |
| Carbon | 76.64 | 79.07 | 81.90 | 83.94 | 81.46 |
| Hydrogen | 5.09 | 4.96 | 5.01 | 4.86 | 5.03 |
| Nitrogen | 1.74 | 1.52 | 1.67 | 1.55 | 1.64 |
| Oxygen (by difference) | 9.83 | 6.88 | 5.00 | 3.73 | 5.43 |
| Gieseler Max Fluidity (log ddpm) | 1.25 | 2.78 | 4.43 | 3.50 | 3.03 |
| Gieseler Fluid Range (Deg.C) | 66.0 | 71.0 | 116.0 | 106.0 | 106 |
| pH (methanol/water) | 4.12 | 8.50 | 8.99 | 7.57 | NA |
| Area under the absorbance peak, carbonyl band (1850-1636 $cm^{-1}$), arbitrary unit | 20.7 | 21.93 | 17.74 | 16.83 | NA |
| Sole-Heated Oven Analysis (at normalized conditions 52 pcf, 2% moisture) | +1.0 | -9.0 | -5.4 | +0.3 | NA |
| Heating Value (cal/gm) | 7618 | 7874 | 8140 | 8084 | 8084 |
| Pilot Oven Carbonization Test | | | | | |
| Coal Mosture (%, db) | 8.5 | 2.9 | 1.7 | 1.9 | 3.7 |
| Coal Grind (%, -3.35 mm) | 82.2 | 86.5 | 89.1 | 91.5 | 85.6 |
| Dry Oven Bulk Density ($kg/m^3$) | 801.0 | 885.0 | 884.0 | 866.0 | 906.0 |
| Max. Oven Wall Presxure (kPa) | 3.7 | 6.7 | 12.9 | 16.3 | 5.9 |
| Coking Time (h)18.4 | 18.4 | 17.3 | 16.2 | 17.1 | 17.0 |
| ASTM Stability | 23.0 | 50.0 | 55.0 | 65.0 | 63.0 |
| NSC Coke CSR | 36.0 | 62.0 | 69.0 | 66.0 | 60.0 |
| NSC Coke CRI | 57.0 | 24.0 | 22.0 | 27.0 | 31.0 |
| Coke Hardness | 71.0 | 67.0 | 68.0 | 71.0 | 72.0 |
| Coke Size (mm) | 50.7 | 61.5 | 72.7 | 69.6 | 66.8 |
| Coke Yield (%) | 67.9 | 69.2 | 76.2 | 79.3 | 72.4 |
| Coke Volatile Matter (%) | 2.2 | 0.9 | 0.9 | 0.9 | 0.6 |

TABLE 2 pH of Size Fractions of Ground +8 mesh Illinois No.6 Coal

| Mesh size | -8 + 24 | -24 + 100 | -100 |
|---|---|---|---|
| Wt% of total | 47.6 | 35.4 | 17.0 |
| pH | 2.88 | 3.00 | 5.36 |

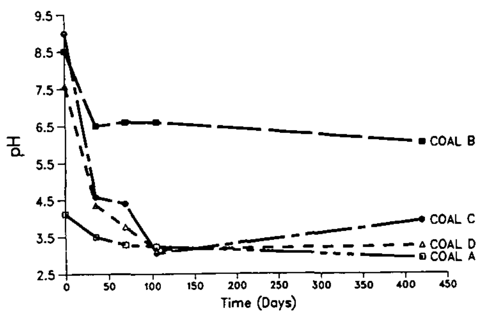


Fig. 1 pH (methanol/water) as a function of coal oxidation time

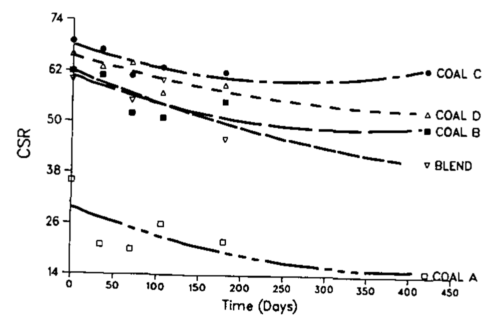


Fig. 2 Effect of coal oxidation time on CSR

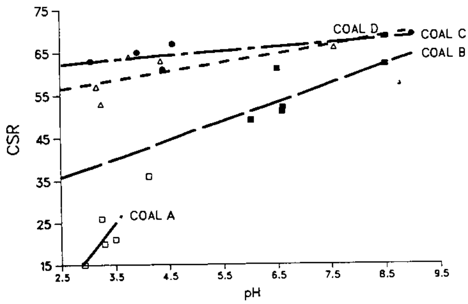


Fig. 3 Oxidation effects indicated through pH (methanol/water) and CSR

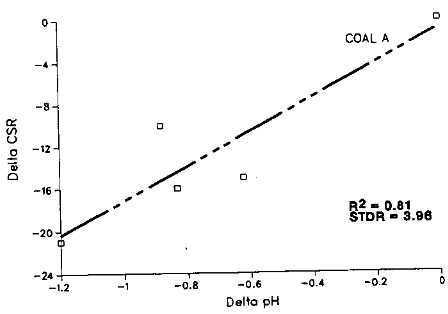


Fig. 4 Use of pH (methanol/water) for assessing CSR loss